First-principles calculations of defect formation energy and charge transition levels of a deep-level defect in wide-gap semiconductors

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In this tutorial, we present step-by-step procedures of first-principles calculation of the defect formation energy of a point defect in a wide-gap semiconductor. We focus on a case, in which a point defect creates localized mid-gap states in the band gap of a wide-gap semiconductor. This type of defect is called a deep-level defect. They are called ‘deep’ because the energy required to remove an electron or hole from the defect to the conduction or valence band is much higher than the characteristic thermal energy of $k_B T$, where $k_B$ is the Boltzmann constant and $T$ is temperature. As a deep-level defect could form multiple defect levels in the band gap, it could behave as an electron or hole trap, implying that a deep-level defect can be present in multiple charge states. Additionally, depending on the number of electrons localized at the defect site and its electronic properties, a deep-level defect can have multiple spin states with open shell configurations. Multiple possible local distortions could also add another complexity for the defect energetics. First-principles total energy calculations could shed a light on the defect thermodynamics and the defect stability. In the rest of this tutorial, we will consider the nitrogen vacancy defect in aluminum nitride (w-AlN) as a prototypical example of a deep-level defect and present calculations of its defect formation energy and the background theory as well. We will also provide several python codes to perform some of these calculations, to plot the defect formation energy, and to extract the charge transition levels of a deep-level defect.

Nitrogen Vacancy in w-AlN.

Let us introduce our model system, which is the nitrogen vacancy ($V_N$) in aluminum nitride with the wurtzite structure (w-AlN). The defect structure is shown in Fig. 1. A nitrogen atom in w-AlN is coordinated with four Al atoms in a $C_{3v}$ tetrahedral geometry. Thus, in the presence of $V_N$, the nearest neighboring Al atoms expose their $sp^3$ dangling bonds toward the vacancy site, which is schematically
shown in Fig. 1. As we will see later, these Al dangling bonds create deep defect levels in the band gap of AlN by forming symmetry-adapted ‘molecular orbitals’.

![N vacancy model](image)

**Figure 1.** An atomistic model of nitrogen vacancy created in a 480-atom orthorhombic supercell of $w$-AlN. A schematic of active Al sp$^3$ dangling bonds created by the formation of VN are shown on the right.

**The Details of Density Functional Calculations.**

We used plane-wave density functional theory to calculate the total energy and the electronic structure of VN in $w$-AlN, as implemented in QUANTUM ESPRESSO. For the exchange correlation part of the density functional, we used the generalized gradient approximation developed by Perdew, Burke, and Ernzerhof. 75 Ry of plane-wave cutoff energy was used along with the ONCV pseudopotentials (PPs) for Al and N, which were generated by Schlipf and Gygi (The sg15 set). The valence configurations of Al and N are 3s$^2$3p and 2s$^2$2p$^2$ for Al and N, respectively. We note that the Al PP used for this work is not the official sg15 ONCV PP of Al, which contains extra 2s$^2$2p$^6$ semi-core states. We compared both the Al PPs with and without the semicore states and checked their results are the same within an accuracy of 10 meV in terms of defect level positions with respect to the valence band edge. For the Brillouin zone sampling, we used the Gamma-only option and checked the use of a 2x2x2 k-point mesh produced the same result. The entire calculation results along with all the input files can be found at /project/gagalli/DATA_COLLECTIONS/hseo/Tutorial_N_vacancy_AlN. We will assume that this is our current, default directory for this tutorial, unless otherwise noted. To simulate an isolated VN, we used a 480-atom supercell model of AlN with one missing nitrogen atom, which is shown in Fig. 1.

**VN in $w$-AlN in different charge, spin, and local defect structures.**

To motivate the defect formation energy calculation, we consider the DFT total energy calculations of VN in various charge, spin, and local defect structures. The defect formation energy will be
needed to compare these total energies. A simple, straightforward calculation of $V_N$ in $w$-AlN would be to simply remove a N atom from the 480-atom orthorhombic supercell of $w$-AlN and run a DFT relaxation at the PBE level of theory. This result can be found in ~/DFT_DATA/q_n0_S1_2 folder, where $q$ means a charge state and $n0$ means negative (n) zero (0). So, $q_n0$ means that no extra charge or electron is added to the supercell and the nitrogen vacancy is in its neutral state ($q = 0$). $S$ indicates its total spin. In the neutral charge state, the N vacancy has total spin of 1/2 and I put the spin information in the folder name as S1_2.

![Electronic band structure of the 480-atom supercell of AlN with a single N vacancy. Red arrows represent electron spins.](image)

Figure 2. Electronic band structure of the 480-atom supercell of AlN with a single N vacancy. Red arrows represent electron spins.

Fig. 2 shows the electronic structure of $V_N$ in the $q = 0$ state. The presence of the neutral nitrogen vacancy introduces several in-gap defect states, which appear as non-dispersive states in the band gap. A N vacancy create three electrons and these three electrons are captured at the N vacancy site. We note, however, that there may be other possible electronic configurations to be considered. For example, by changing the doping level of the host, one might lower the Fermi level below the $a'(2)$ state. Then the N vacancy would be positively charged by transferring an electron from the $a'(2)$ state to the Fermi level. Similarly, the N vacancy could be negatively charged by raising the Fermi level. These positively charged and negatively charged situations can be simulated by introducing an extra +1 charge (a hole) and -1 charge (an electron) to the supercell, respectively. The simulation results can be found in the q_p1_S0 ($p$ means positive.) and q_n1 folders. Note that there are two results for the negative charge state:
It means that there are two stable local minima for the negative charge states: one with a total spin 1 and the other one with a total spin 0. The two local minima have two different defect structures, which I labeled as C1h_f and C1h_s. The reason for the presence of the two local minima are explained in our Scientific Reports paper published in 2016. For the same reason, one can further consider q_n2, q_n3, q_p2, q_p3, etc. Their total energies along with their total spin are summarized in Table 1.

Table 1. Total energies (E), spin states (S), and local point group symmetries of the N vacancy in w-AlN in various charge states (q) calculated at the PBE level of theory.

<table>
<thead>
<tr>
<th>Charge state (q)</th>
<th>S</th>
<th>E (Ry)</th>
<th>Point group</th>
</tr>
</thead>
<tbody>
<tr>
<td>+3</td>
<td>0</td>
<td>-6566.6111</td>
<td>C3v</td>
</tr>
<tr>
<td>+2</td>
<td>1/2</td>
<td>-6566.0444</td>
<td>C3v</td>
</tr>
<tr>
<td>+1</td>
<td>0</td>
<td>-6565.4926</td>
<td>C3v</td>
</tr>
<tr>
<td>0</td>
<td>1/2</td>
<td>-6564.7309</td>
<td>C1h</td>
</tr>
<tr>
<td>-1 (1)</td>
<td>1</td>
<td>-6563.9480</td>
<td>C1h</td>
</tr>
<tr>
<td>-1 (2)</td>
<td>0</td>
<td>-6563.9555</td>
<td>C1h</td>
</tr>
<tr>
<td>-2</td>
<td>3/2</td>
<td>-6563.1507</td>
<td>C3v</td>
</tr>
</tbody>
</table>

The question is how to compare these total energies in Table 1. One cannot directly compare them to determine which charge state is the lowest-energy ground state of VN because different charge states have different number of electrons. In the DFT calculations for these different charge states, different compensating background charge densities were added to make the calculations converge. As noted above, different charge states may have different stability as a function of the Fermi level. In addition, if we want to compare the stability of N vacancy to other types of defects, such as divacancy or impurity-vacancy complexes, then we also need to take into account the difference of number of atoms in the energy comparison. The defect formation energy provides a tool for these energy comparisons.

In general, the defect formation energy is defined as a difference of the defect and the host free energies.

\[
\Phi^D - \Phi^H = \left[ F^D - \sum_i^n \mu_i \right] - \left[ F^H - \sum_i^n \mu_i \right] = F^D - F^H - \sum_j n_j \mu_j + q \mu_e, \tag{1}
\]

where \( F^D \) and \( F^H \) are the Helmholtz free energies of the defect and the host, respectively. \( \mu_j \) is the chemical potential of the \( j \)-type defect (impurity or vacancy). \( q \) is the charge state of the defect and \( \mu_e \) is
the chemical potential of an electron, which is the Fermi level. There may be temperature-related contributions to each free energy, but we assume that they would significantly cancel between $E^D$ and $E^H$. So, we only consider the total energy contributions, which can be directly obtained from DFT calculations. However, in the DFT total energy with a charged defect, there are several artificial energy contributions added from the interactions between a charged defect and its periodic images and between a charged defect and a compensating background charge density. Thus, we need to add correction terms in Eq. (1) and the resultant equation is given in Eq. (2):

$$E_f^D(q, E_F) = E^D + E^D_{corr}(q) - E^H - \sum n_i \mu_i + q(E_F + E_V - \Delta V_{0/b}),$$

(2)

where $E^D$ and $E^H$ are the total energies of the defective supercell and the defect-free host supercell, respectively. $E^D_{corr}(q)$ is the correction term for the artificial interaction energies described above. $n_i$ is the number of missing atoms in the defective supercell and $\mu_i$ is the chemical potential for the missing atom. For a nitrogen vacancy $n_i = -1$. For foreign impurities, $n_i$ is a positive number. We note that the electron chemical potential, which is $\mu_e$ in Eq. (1) is expressed as $q(E_F + E_V - \Delta V_{0/b})$ in Eq. (2), where $E_F$ is the Fermi level, $E_V$ is the valence band maximum, and $-\Delta V_{0/b}$ is a potential alignment term between the defect-free supercell and the supercell with a neutral defect. Below, we will explain the origin of the correction terms and how to calculate each term in Eq. (2) as well.

$E_D$. This is the total energy of a defective supercell. We use the values reported in Table 1. The data can be found at ~/DFT_DATA. If there are several local minima for a given charge state, we use the lowest-energy solution.

$E_H$. This is the total energy to a pristine supercell. One can use the same supercell without any defect. The data can be found at /DFT_DATA/Defect_free_supercell.

$E_V$. This is the valence band maximum. One can read it from the result of the defect-free supercell calculation.

$E_F$. This is the Fermi level, which is referenced to the valence band maximum. We treat this as a theoretical parameter that can be changed from the valence band top ($E_F = 0$) to the conduction band minimum ($E_F = \text{the band gap}$).

$q$. This is the charge state of a defect. It is negative for extra electrons added to the supercell and positive if electrons are removed from the supercell.

$\Delta V_{0/b}$. This term is a potential alignment term between the pristine bulk supercell and the defective supercell (with a N vacancy in it) without any extra charge. In Figure 3, we show the planar
average of the DFT potential energy difference between the defective and defect-free supercells as a function of z in the [0001] direction of AlN: $V_{DFT}^{N}(V_N, q = 0) - V_{DFT}^{bulk}$.

Figure 3. Potential energy difference between the defect-free supercell and the defective supercell with a neutral N vacancy: $V_{DFT}^{N}(V_N, q = 0) - V_{DFT}^{bulk}$. The N vacancy is placed at around $z = 15$ Å.

In Fig. 3, the N vacancy is placed at around $z = 15$ Å, where a sharp peak appears. Moving away from the defect site, the potential difference becomes flat as expected. However, the potential difference does not become exactly zero, but becomes about -14 meV. This means that far from the defect site, the valence band top of the defective supercell is shifted by -14 meV compared to that of the pristine bulk supercell. Note that we will remove electrons from the defective supercell or add electrons to it, but the chemical potential for an extra charge is referenced to the valence band top of the pristine bulk supercell. So, we should correct this discrepancy by adding $\Delta V_0/b$ in the defect formation energy as done in Eq. (2). But, there is an important note for the sign. The DFT potentials ($V_{DFT}^{N}$) shown in Fig. 3 is for an electron. Thus, one should multiply it by -1 to convert it to a normal electrostatic potential ($V$). That is why there is a - sign in front of the $\Delta V_0/b$ term in Eq. (2).

$E_{corr}^D(q)$. This term is a correction term for $E^D$. We will first review the basic theory behind $E_{corr}^D(q)$ and then present how to calculate it. Fig. 4a shows a schematic of a charged defect calculation using the supercell method within the periodic boundary condition. Note that if an extra electron (or hole) is added to a supercell with a deep-level defect, a homogeneous background charge is automatically added in order to neutralize the supercell. Otherwise, the calculation would not converge. Furthermore, we use the periodic boundary condition, thus the extra electron localized at the defect site could interact with its periodic images through the long-range Coulomb interaction. We note, however, the real situation
that we aim to simulate is an isolated charged defect, which is schematically shown in Fig. 4b. $E_{corr}^D(q)$ is applied to $E^D$ to correct both the artificial effects and it is expressed as follows:

$$E_{corr}^D(q) = E_{isolated}(q) - E_{periodic}, \quad (3)$$

where $E_{isolated}$ is the energy of an isolated charge density (Fig. 4b) and $E_{periodic}$ is the artificial energy per supercell induced by the periodic charge images and the background charge density.

**Figure 4.** (a) A schematic for a supercell calculation with a charged defect within the periodic boundary condition. (b) A schematic for the real situation of an isolated charged defect in a homogeneous dielectric medium.

To understand $E_{periodic}$ in Eq. (3) further in details, we may express the electrostatic potential generated by a negatively charged N vacancy in the AlN supercell as follows:

$$V(V_N, q = -1) = V(V_N, q = 0) + V(long-range) + V(short-range) + \Delta V_{-1/0}, \quad (4)$$

where $V(V_N, q)$ is an electrostatic potential of $V_N$ in a charge state of $q$, $V(long-range)$ is a long-range screened Coulomb potential generated by the periodic charges, $V(short-range)$ is a short-range potential induced by atomic relaxation and other quantum effects around the defect, and $\Delta V_{-1/0}$ is a global potential shift added by the code to ensure the total average of the $V(V_N, q = -1)$ to be zero. We note that $V(long-range)$ is the origin of the artificial electrostatic energy of the periodic array of the localized charge density. We can calculate this electrostatic energy by using a periodic array of a localized model charge density (e.g. Gaussian) with a neutralizing background in a dielectric medium ($\epsilon$).

$$E_{lattice} = \frac{1}{2} \int \rho_p(r)V_{long-range} (r) dr, \quad (5)$$

where $\rho_p(r) = \sum_R [q_d(r - R) + n(r - R)]$, and $-\nabla^2 V_{long-range} = \frac{4\pi}{\epsilon} \rho_p(r)$. $\rho_p(r)$ is the periodic Gaussian charge density ($q_d(r)$) defined on a Bravais lattice ($R$) with a neutralizing charge background ($n$).
By solving the Poisson equation, one can obtain the $V_{\text{long-range}}$ potential. One can perform these calculations in the Fourier space, and the result is given as follows.

$$E_{\text{isolated}} - E_{\text{lattice}} = \frac{1}{\pi \epsilon} \int_{0}^{\text{cut}} |q_d(g)|^2 dg - \frac{2\pi}{\epsilon \Omega} \sum_{g \neq 0} |q_d(g)|^2 \frac{1}{G^2}$$

(6)

We note, however, there is an extra, artificial interaction to be taken care of, which is the interaction energy between $V$(short-range) and the homogeneous background, called $E$(short-range). For this calculation, we can use Eq. (4). Note that the total average potentials of $V(N, q)$ and $V$(long-range) are zero. Therefore, we have

$$E_{\text{short-range}} = -q \frac{1}{\Omega} \int_{\Omega} V_{\text{sr}}(r)d\mathbf{r} = q \frac{1}{\Omega} \int_{\Omega} \Delta V_{-1/0} \mathbf{r}d\mathbf{r} = q\Delta V_{-1/0}.$$  

(7)

Therefore, the short-range, artificial interaction energy can be calculated by finding the global potential shift, $\Delta V_{-1/0}$. Then, how do we calculate this? We can rearrange Eq. (4) as follows,

$$\Delta V_{-1/0} = V(N, q = -1) - V(N, q = 0) - V(\text{long} - \text{range}) - V(\text{short} - \text{range}).$$

(8)

We further note that $V$(short-range) is localized near the defect site, meaning that it goes to zero far from the defect. Therefore,

$$\Delta V_{-1/0} = [V(N, q = -1) - V(N, q = 0)]_{\text{far}} - V(\text{long} - \text{range})_{\text{far}}.$$  

(9)

Finally, we can combine this short-range energy term with the $\Delta V_{0/b}$ term described above as $\Delta V_{-1/b}$. Therefore, the final form of the corrected defect formation energy can be written as follows:

$$E_f^D(q, E_F) = E^D - E^H - \sum n_i \mu_i + q(E_F + E_V) + E_{\text{corr}}^{\text{FNV}}(q),$$

where

$$E_{\text{corr}}^{\text{FNV}}(q) = E_{\text{isolated}} - E_{\text{lattice}} - q\Delta V_{-1/b}.$$  

(10)

FNV in Eq. (11) stands for Freysoldt, Neugebauer, and Van de Walle, who developed this method.

We now turn to how to calculate terms in Eq. (11). We will use the program that is called ‘sxdefectalign’ to perform the model calculations and the potential alignment. The files can be found at [https://sxrepo.mpie.de/projects/sphinx-add-ons/files](https://sxrepo.mpie.de/projects/sphinx-add-ons/files). I also put the executable file in the Tutorial folder. One drawback of using this sxdefectalign code is that it does not support the XSF file format, which Quantum Espresso uses to produce the potential file. So, I wrote a simple code to convert the XSF potential file generated by QE to the VASP potential format, which this sxdefectalign code supports. The code is named as XSF_to_LOCPOT.cpp and it can be found in the tutorial folder.
Once the potential files are generated for inputs to the sxdefectalign calculations, there is one more ingredient that needs to be calculated, which is the static dielectric constant of the lattice. One can calculate it using Quantum Espresso using various ways, which are not covered in this Tutorial. I have calculated the static dielectric constant by using the finite E-field method, which is described in Umari and Pasquarello, PRL 89, 157602 (2002) and Souza, Iniguez, and Vanderbilt, PRL 89, 117602 (2002). The results are summarized in Table 2.

Table 2. Calculated high-frequency and static dielectric constants of w-AlN at the PBE level of theory.

|                  | $\epsilon_{\infty,||}$ | $\epsilon_{\infty,\perp}$ | $\epsilon_{0,||}$ | $\epsilon_{0,\perp}$ |
|------------------|------------------------|---------------------------|------------------|---------------------|
| Theory (this work) | 4.42                   | 4.63                      | 8.33             | 9.77                |
| Experiment       | 4.13                   | 4.27                      | 8.5(poly-crystalline) |                      |

Note that w-AlN is an anisotropic material whose dielectric response differs depending on the axis. We use their harmonic mean for the defect formation energy calculations, which is 8.76. With the potential files and the dielectric constants at hands, we can run the sxdefectalign code as follows:

```
./sxdefectalign --ecut 80 --gstep 0.00001 --beta 1 --gamma 1 --expnorm 0 --printRho --charge 1 --eps 8.76 -a3 --center 0.5,0.6111,0.722 --relative --vref LOCPOT_defect_free --vdef LOCPOT_q_n1_50 --cellFromPot --vasp --printPot
```

Each term such as ecut, gstep, etc. is explained in the sxdefectalign manual. Once the program is successfully run, a few files are generated (e.g. vline-eV.dat) along with a text output:

```
cell = [a1=[ 29.5404 , 0 , 0 ],a2=[ 0 , 30.6994 , 0 ],a3=[ 0 , 0 , 37.8898 ]
ng=415108
VASP mesh: 180 x 180 x 216
multiplicity = 1
VASP mesh: 180 x 180 x 216
multiplicity = 1
vAlign=0 eV
eAlign=0 eV
Isolated energy : 0.398942
Periodic energy : 0.356127
Difference (Hartree) : -0.0428148
Difference (eV) : -1.16505
Defect correction (eV): 0.133062 (incl. screening & alignment)
```

In this log file, the isolated energy is ‘unscreened’ $E_{\text{isolated}}$ in Eq. (11) written in Hartree, which is the electrostatic self-energy of a single Gaussian charge density. The periodic energy is ‘unscreened’ $E_{\text{lattice}}$ in Eq. (11). The defect correction is (Isolated energy - Periodic energy)/$\epsilon$, which is now the same as $E_{\text{isolated}} - E_{\text{lattice}}$ in Eq. (11).
To calculate the last potential alignment term in Eq. (11), one needs to compare the potentials from the DFT calculations and the model calculation, far from the defect site.

\[ \Delta V_{-1/b} = [V(V_N, q = -1) - V(bulk)]_{\text{far}} - V_{\text{far}}(\text{long-range}). \]  

These potentials are written all together in the vline-\text{eV}.dat. I have written a python script (written in Python 3) to separate out and plot each potential. It is a class in a python module named ‘defects.py’). Once imports the defects.py module, one can execute it as follows:

```python
In [37]: from defects import *
In [38]: sxdefectalign_plot('vline-eV.dat')
```

Then, one obtains a png file, named potentials_plot.png and it is shown in Fig. 5.

**Figure 5.** The electrostatic potentials for the defect potential alignment.

In Fig. 5, the green line corresponds to \([V(V_N, q = -1) - V(bulk)]\) obtained from the DFT potentials and the blue line is the model potential. Their difference, which is the red line is the sum of the short-range potential and the global potential shift. As discussed previously, the short-range potential is supposed to decay to zero far from the defect, which is positioned at around \(z = 25 \sim 30\) Bohr in Fig. 5. Indeed, one can see that the red line in Fig. 5 shows a strong oscillation pattern near the defect site and it decays into a ‘flat’ region at around \(z = 5 \sim 10\) Bohr. So, we read off the value at this flat region or an average value around this region, which is -0.014 eV. There is an important note for the sign. The DFT potential shown in Fig. XX is the electrostatic potential for an electron. So, one need to multiply -0.014 eV by -1 to convert it to the usual electrostatic potential. So, \(-q\Delta V_{-1/b}\) in Eq. (11) is given as \(-1*(-1)*(-0.014\ \text{eV}) = 0.014\ \text{eV}\). Finally, the entire correction term in Eq. (11) becomes 0.133062 eV (E_{isolated} -
\[ E_{\text{lattice}} + 0.014 \text{ eV} (q = -1) = 0.147062 \text{ eV} \] for the negatively charged \((q = -1)\) nitrogen vacancy in AlN.

\(\mu_i\). This is the chemical potential for a missing atom or an impurity atom in the defective supercell. We will consider several possible bulk compounds to determine the boundary conditions for them. These energies are found in the Tutorial folder. For the N vacancy in AlN, we need the total energies of the AlN bulk, the \(N_2\) molecule, and the Al metal. The boundary condition for the N chemical potential can be determined by considering the following equations.

(1) In the AlN supercell, AlN is obviously a stable thermodynamic phase.

\[ \mu_{\text{Al}} + \mu_N = \mu_{\text{AlN, bulk}}. \tag{13} \]

(2) In the AlN supercell, we don’t want metallic Al cluster to precipitate.

\[ \mu_{\text{Al}} \leq \mu_{\text{Al, bulk}}. \tag{14} \]

(3) We don’t want to lose N atom from the supercell.

\[ \mu_N \leq \frac{1}{2} \mu_{\text{N}_2 \text{ molecule}}. \tag{15} \]

By combining (13), (14), (15), we obtain the following boundary condition for the N chemical potential.

\[ \mu_{\text{AlN, bulk}} - \mu_{\text{Al, bulk}} \leq \mu_N \leq \frac{1}{2} \mu_{\text{N}_2 \text{ molecule}}. \tag{16} \]

In Eq. (16), we see that the N-poor condition is determined by the energy difference between the AlN bulk and Al metal, while the N-rich condition is determined by half of the \(N_2\) molecule energy.

With all these values (e.g. the total energies, the chemical potentials, and the correction terms) at hands, we can calculate the defect formation energy as a function of the Fermi level, plot the formation energy, and calculate the charge transition levels. These calculations can be also done using the python script that I wrote.

To calculate the defect formation energy, one need to write an input file, called N_vac_N_poor.in, in which N_poor means we are in the nitrogen-poor limit for the N chemical potential.

---

```
#Input file for defect formation energy calculations
#So far, I only consider defects in mono-atomic or binary crystals.
#Defects could be impurity, mono- or di-vacancy, and their complexes

&VBM
   # valence band maximum(eV)
   6.9696
```
&band_gap #with respect to the VBM (eV) 5.0

&Host_type
Al N

&Vacancies #For example, for divacancy in AlN, put 'Al N' N

&Impurities


&Host_supercell_energy #(Ry) -6585.061221

&Charge_state_range #two integer numbers // make sure you have a right number of alignment term -2 2

&Defective_supercell_energy #charge_state(q) and energy (Ry) -2 -6563.150785 -1 -6563.955569 0 -6564.730914 1 -6565.492659 2 -6566.044454

&Correction_terms #(eV), for each charge state (e.g. -2 to 2): short-range potential energy, and (E_iso - E_periodic) -0.016 0.532248 -0.014 0.133062 0 0 -0.013 0.133062 -0.023 0.532248

With this input file, one can run the following,

In [39]: calculate_E_formation('N_vac_N_poor.in')

Then, one obtains a png file, which is shown in Fig. 6, along with two more text files. Fig. 6 contains the defect formation energy of V_N in various charge states; q = -2 to q = 2. As apparent in the definition of the defect formation energy, the defect formation energy is a linear function of the Fermi level and different charge states correspond to different slopes. Therefore, an important information that one can extract from this plot is which charge state is the ground state for a given Fermi level. For example, with a Fermi level near the conduction band (strongly n-type AlN), V_N with two extra eletrons (q = -2) would be the ground state while V_N in the q = +2 state would be the ground state in a strongly p-type AlN. So, one could take
the lowest energy value for a given Fermi level and draw only one line (with several kinks) as the defect formation energy of V\(_N\) in w-AlN. In Fig. 6, it is shown as a bold black line. This data is also written in a separate text file, named N_vac_N_poor.in_out.

**Figure 6.** The defect formation energy of V\(_N\) in AlN in various charge states as a function of the Fermi level.

In Fig. 6, there are several points where the defect formation energies of two different charge states are degenerate, which are marked with blue dots. These are called the charge transition levels and are written in a separate file, named N_vac_N_poor.in_CTL.